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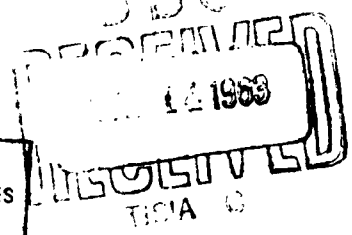CAMERON STATION. ALEXANDRIA. VIRGINIA

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Research in

MOLECULAR QUANTUM THEORY

Final Technical Report

on

Contract Number DA-91-591-EUC-2034 (OI-26235-B)

with the University of Keele, England.

30th November, 1962

Report for the period 1st November, 1961 - 31st October, 1962

1. GENERAL SURVEY

During the period 1st November, 1961 to 31st October, 1962, work has continued on the following projects:

1.1) General Many-Electron Theory

The method of generalized product functions, developed in previous Reports and publications, has been extended in two directions. First, the strong orthogonality condition on the functions describing different electron groups has been relaxed, in the two-group case, and the consequences of non-orthogonality are being investigated in detail. Secondly, it has been shown that when one of the two group functions belongs to a finite subspace of Hilbert space (e.g. an antisymmetrized orbital product), the results easily reduce to those of Sinanoglu and Szasz. Some attention is now being given to the determination of optimum pair functions to describe pair correlations.

On the other hand, the general case of two non-orthogonal groups is sufficiently important to merit further development: it is of special importance when the two electron groups (A and B, say) are in non-singlet states, for there is then a non-trivial spin-coupling problem and this lies at the root of theories of ferromagnetic and anti-ferromagnetic coupling. Considerable progress has been made in this area and it has been shown that the Heisenberg coupling is the first term of a spin Hamiltonian representing the interaction energy in powers of the spin scalar product $S^A.S^B$.

Actual applications of generalized product functions are discussed in other sections.

1.2) Calculations on Atoms

Work on the sequence of beryllium-like systems, Li^-, Be, B^+,....

has been concluded and a paper has been submitted for publication. The

calculations suggest that the electronic structure of atoms can be well

represented by a wave function of the form:

$$\Psi(1,...N) = \mathcal{A}\left[\Psi_A(1,...N_A) \Psi_B(N_A+1, ...N_A+N_B) ....\right]$$

where the various factors describe the K, L, M,....shells and may individ-

ually admit electron correlation. This work is fully described in Special

Technical Report STR No. 1 (1st Sept. 1962).

1.3) Calculations on Molecules

Work on the NH_2 radical has been concluded and papers are in

preparation for publication: the work has already been described in detail

in STR No. 2 (15th Sept. 1962). The calculations have been concerned

mainly with the spin density, which determines the hyperfine coupling

constants, and a variety of methods have been employed. These include the

unrestricted Hartree-Fock method (with and without spin projection to a

doublet state) and the configuration interaction method referred to in

the Final Technical Report (30th Nov. 1961) on the previous contract.

Non-empirical calculations on small organic molecules (e.g. formal-

dehyde) are being continued, with a view to development of satisfactory

semi-empirical methods for dealing with much larger molecules, both

saturated and unsaturated. This involves the detailed treatment of the

σ electrons, and a group-function approach (each localized σ bond

being a "2-electron group") seems to offer considerable promise. Owing to

uncertainties in the values of many-centre 2-electron integrals, it has

been necessary to start the systematic development of integral programmes for electronic computation. Progress has consequently been slow, but when all programmes are operating it should be possible to deal very rapidly with a number of interesting molecules.

An investigation of steric effects in small molecules is also dependent on the availability of integral values. The calculations have however been pressed to a point at which the main factors determining inter- and intra-molecular repulsions are becoming evident. In this work a simplified model, consisting of two hydrogen molecules (representing two neighbouring bonds) is being considered in great detail.

Finally, work on approximate self-consistent field theory, as applied to the π electrons of conjugated systems, has continued. One notable advance has been the development of perturbation methods which preserve self-consistency up to first order in the wave function (third order in the energy). With such methods, it is possible to define atom and bond polarizabilities, analogous to those used in Hückel theory, which permit the discussion of substitution effects within the framework of a self-consistent, many-electron theory.

1.4) Electronic Computation

During the period under review, much time has been devoted to programme development. Programmes now include integral computation (so far up to three centres only), matrix transformations describing change of basis etc., self-consistent field calculations, and various steepest descent and matrix techniques. The "Mercury" computer used so far will shortly

be replaced by the "Atlas" and the whole computational situation has had
to be reviewed. The Quantum Theory Group is to obtain its own small
computer (IBM 1620), as a result of generous support from the NATO Research
Grants Programme, and arrangements are being made for use of a much larger
machine (English Electric "KDF 9"), close to this University, when
necessary. Consequently, programming will presently be switched from
"Autocode" to "Fortran" and considerable redevelopment and reorganization
will be necessary.

Work Concluded or Published (1st Nov., 1961 - 31st Oct., 1962)

1) Ring Currents in Aromatic Molecules. I. J. Maddox and R. McWeeny,
   J. Chem. Phys., 36, 2353.

2) Perturbation Theory for the Fock-Dirac Density Matrix, R. McWeeny,
   Phys. Rev., 126, 1028.

3) Quantum Organic Chemistry, R. McWeeny, Ann. Rep. Chem. Soc., (Lond.) 1961.

4) Bond-Length Alternation in Heterocyclic Ring Systems, D. J. Davies,
   Nature, 194, 82.

5) Conformazione Molecolare di Polimeri Lineari in Soluzione, V. Magnasco,
   La Scuala in Azione (Periodical of Inte Nazionale Idrocarburi, Italy).

6) An Empirical Method for Calculating Barriers to Internal Rotation in
   Simple Molecules. V. Magnasco, Nuovo Cimento 24, 425.

7) Poly(ethylene oxide) in Solution, (C. Rossi) and V. Magnasco. J. Polymer
   Sci., 58, 977, (1962).

8) The Density Matrix in Many-Electron Quantum Mechanics Pt. III.
   Applications to the beryllium atom and 4-electron ions. R. McWeeny
   and B. T. Sutcliffe (Submitted for Proc. Roy. Soc.,).

9) Spin Polarization Effects in Paramagnetic Molecules, A Calculation on the NH_2 Radical. R. McWeeny and B. T. Sutcliffe, Mol. Physics (to be published) (See also STR No. 2, 15th Sept., 1962).

10) Unrestricted Hartree-Fock Calculations on the NH_2 Radical, B. T. Sutclif (to be published) (See also STR No. 2, 15th Sept. 1962).

11) /Stark Effect in Hydrogen, E. Steiner, J. Chem. Phys., 37, 454.

12) /Classical and Continuum Contributions to Polarizability and Force · Constants, (W. Byers Brown and) E. Steiner, J. Chem. Phys., 37, 461.

2. SCIENTIFIC WORK

In this section we give full abstracts of recently published papers and Special Technical Reports relating to work concluded during the period 1st November, 1962 - 31st October, 1962, along with more detailed accounts of work still in progress. The work in progress will be continued during the contract period commencing 1st November, 1962.

2.1) Wave Functions for Beryllium and 4-Electron Ions

The group-function method, and the forms of the inner-shell and outer-shell functions, were summarized in the Final Technical Report (30th November, 1961) on the previous contract. The whole investigation has now been described in detail in STR No. 1 (1st September, 1962) and a paper has been submitted for publication. At this point, therefore, we merely recall the results for the beryllium atom, these being typical.

/ Not performed on contract

The calculated total energies (in Hartree atomic units), with and without the restriction of strong orthogonality between inner and outer shells, are compared below with the results of the one-determinant calculation (Slater orbitals) with Hartree-Fock calculations, and with the virtually exact values obtained from exceedingly large variational calculations.

1 Determinant	H-F	Orthogonal Groups	Non-Orthogonal Groups	Exact
-14.556	-14.573	-14.611	-14.621	-14.667

It is seen that removal of the strong orthogonality requirement leads to no great improvement of the group-function results, although it introduces tremendous complications into the calculation. This is encouraging and lends support to the belief that systems with separate parts can be accurately described by using an antisymmetrized product of group functions. The variational calculation, in which each group is made self-consistent in the field produced by all other groups, was found to be both convenient and rapidly convergent. The electron correlation introduced within each group was investigated by calculating the pair function for electrons of opposite spin and comparing this with the (uncorrelated) product approximation. The resultant "correlation holes" (radial in the inner shell, angular in the outer shell) were plotted and discussed.

2.2) <u>Spin Density in the NH$_2$ Radical</u>

Calculations of the spin density, using a variety of methods and approximations, have been fully reported in STR No. 2 (15th Sept. 1962). Here we briefly summarize the methods and results obtained.

There are basically two approaches (i) using configuration interaction and (ii) using unrestricted Hartree-Fock functions. All calculations were performed with two alternative choices of orbital basis, Slater AO's and numerical SCF AO's.

(i) <u>Configuration Interaction Calculations</u>

A wave function is constructed along the lines of McWeeny and Ohno[1] from the nitrogen orbitals 1s, 2s, $2p_x$, $2p_y$, $2p_z$ and the hydrogen orbitals h_1 and h_2. The valence orbitals are Schmidt orthogonalized against the nitrogen inner shell and then hybridized (roughly trigonally) so that two hybrids, t_1 and t_2, point directly towards the hydrogens (with orbitals h_1, h_2), the third being associated with the lone pair. The resulting orbitals are then orthogonalized symmetrically, among themselves, in order to provide for the construction of strong-orthogonal functions for the various electron groups. The groups and the orbitals used in describing them are then as follows

Group	A	S	B$_1$	B$_2$	L	(4.1)
Orthogonal AO's	$2p_z$	1s	t_1, h_1	t_2, h_2	t_3	

The bond orbitals employed are

$$B_i = \cos\theta\ t_i\ +\ \sin\theta\ h_i \quad \text{(bonding)} \quad (i = 1,2)$$

$$\bar{B}_i = \sin\theta\ t_i\ -\ \cos\theta\ h_i \quad \text{(antibonding)} \tag{4.2}$$

The 'ground state' of each bond is then described by

$$B_i(1)B_i(2) \quad \Theta_{oo}(1,2) \tag{4.3}$$

while the lowest triplet states are

$$[B_i(1)\bar{B}_i(2)-\bar{B}_i(1)B_i(2)]\ \Theta_{1m}(1,2) \quad (m = -1,0,1) \tag{4.4}$$

Here Θ_{sm} is the spin function corresponding to spin eigenvalues s,m.
The triplet functions of each bond may be coupled with the odd electron to
give an excited doublet function for the whole molecule and this mixes with
the one-configuration ground state, putting spin density into the bond. This
is the mechanism invoked by several authors (e.g. McConnell and Chestnut[2]),
which has been treated elsewhere in a very general way.[3]

The experimentally observed quantity is the coupling constant J_n
which appears in the part of the spin Hamiltonian linear in the nuclear
spins, namely

$$\sum_n h\ J_n \mathbf{j}_z(n)$$

This is related to the spin density at nucleus n by

$$J_n = \frac{e^2 h g g_n}{3 m M_o c^2}\ Q_1(1_n)$$

where $Q_1(1_n)$ denotes the diagonal element $(1' = 1)$ of $Q_1(1;1')$, evaluated
at nucleus n. If the electronic g factor is taken to be 2.0023 and the

spin density is measured in atomic units of volume^{-1}, this becomes

$$J_n \approx 400.12 \; g_n \; Q_1(1_n) \qquad \text{Mc/sec}$$

The nuclear g values assumed are[4]

$$g_n \; \text{(hydrogen)} = 5.58540 \qquad g_n \; \text{(nitrogen)} = 0;40357$$

and when these values are used the results listed in Table 1 are obtained.

Table.1 Coupling Constants (CI)

		Slater AO's	SCF AO's	Experimental	
Nitrogen	J_n	22.3	11.5	14.45	Mc/sec
Hydrogen	J_n	-38.8	-22.8	(-) 33.52	Mc/sec

(ii) Unrestricted Hartree-Fock Calculations

In this approximation the electrons are divided into an α-spin group and a β-spin group, and we take

$$\Psi(1,\dots N) = \mathcal{A} \left[\Psi_\alpha (1,\dots N_\alpha) \; \Psi_\beta (N_\alpha+1, \dots N) \right]$$

where Ψ_α, Ψ_β are usually antisymmetrized orbital products. The spin density is simply

$$Q_1(1) = P_\alpha (1) - P_\beta (1)$$

where, for example, $P_\alpha (1)$ denotes the diagonal element of the spinless density matrix $P_1(1;1)$ for electrons of spin $+\frac{1}{2}$. The variational methods

for detemining Ψ_α and Ψ_β (without orthogonality restrictions on the orbital factors) are well known: they comprise the "unrestricted Hartree-Fock" approach. The coupling constants detcmined in this way are given in Table 2.

Table 2. Coupling Constants (UHF)

	Slater AO's	SCF AO's	Experimental	
Nitrogen	75.2	39.4	14.45	Mo/sec
Hydrogen	-35.3	-25.0	(-) 33.52	Mo/sec

One major disadvantage of this approach is that the functions used is not a pure doublet, and it is not yet clear how important the contamination by functions of higher multiplicity may be. Another awkward feature is the "splitting" of the 1s core orbitals, which recognizes electron correlation in the core (decreasing the variational energy) at the same time as any "spin polarization" effects. Strictly the two effects should be independent, and some of the core splitting (which appears as the difference of two very large quantities and is therefore difficult to calculate accurately) may in fact by spurious. Two modifications were therefore investigated: first, the "freezing" of the core (α and β electrons being given the same 1s orbital: and, secondly, projection of the one-configuration function to a pure doublet state. The first modification was of limited importance. But the second yielded rather different results:

$$J(\text{nitrogen}) = 26.2 \qquad J(\text{hydrogen}) = -16.7 \quad (\text{SCF AO's})$$

The spin contamination by higher multiplets is therefore a very serious factor. This contamination should of course be removed _before_ the variational calculation but this leads to many difficulties. One great advantage of the configuration interaction method is that these difficulties are avoided from the start.

References

1) R. McWeeny and K. Ohno, Proc. Roy. Soc., A 255, 367, (1960).

2) H. M. McConnell and D. B. Chestnut. J. Chem. Phys., 28, 107, (1958).

3) R. McWeeny, Preprint No. 57, Quantum Chemistry Group, Uppsala University (15th Nov. 1960).

4) J. Pople. W. Schneider and H. Bernstein "High Resolution Nuclear Magnetic Resonance". (McGraw Hill, 1959)

2.3) Group-Function Calculations on Small Molecules

McWeeny and Ohno[1] have shown that in the case of the water molecule the results of LCAO-MO SCF calculations can easily be surpassed in accuracy by using an antisymmetrised product of group functions and including CI within each of these group functions. The aim of the work described here is to extend these calculations to other small molecules and to investigate the possibility of a semiempirical development which would make the method applicable to larger molecules.

The starting point for these calculations is a basis of orthogonalized atomic orbitals, so chosen as to emphasize the localization of σ-bonds and lone-pair electrons. The total wave function is then given by

$$\Psi(1,2,\ldots.N) = M \sum_{\mathcal{P}} (-1)^P \psi_A(1,2)\, \psi_B(3,4)\ldots \tag{1}$$

where the two-electron function describing a localized σ bond (R) is

$$\psi_R'(1,2) = c_1^R \Phi_1^R(1,2) + c_2^R \Phi_2^R(1,2) + c_3^R \Phi_3^R(1,2)$$

with

$$\Phi_1(1,2) = (\phi_1 \bar{\phi}_1)$$
$$\Phi_2(1,2) = 2^{-\frac{1}{2}}\left\{ (\phi_1 \bar{\phi}_2) + (\phi_2 \bar{\phi}_1) \right\}$$
$$\Phi_3(1,2) = (\phi_2 \bar{\phi}_2)$$

$$\left. \right\} \tag{2}$$

where

$$\phi_1(1) = 2^{-\frac{1}{2}}\left\{ \chi_a(1) + \chi_b(1) \right\}$$
$$\phi_2(1) = 2^{-\frac{1}{2}}\left\{ \chi_a(1) - \chi_b(1) \right\}$$

Here $(\phi_i \bar{\phi}_j)$ stands for $2^{-\frac{1}{2}} \det [\phi_i(1)\alpha(1)\, \phi_j(2)\beta(2)]$ and χ_a and χ_b are orthogonal AO's on atom a and b respectively.

The total electronic energy can then be written as

$$E_{\Psi} = E_{\Psi - R} + E_R,$$

where $E_{\Psi - R}$ is the total electronic energy of the system with group R removed, while E_R is the energy of group R in the field provided by the rest of the molecule. E_R is obtained by solving a 3 x 3 secular equation, the matrix elements of which can be derived in the usual way in terms of

$$I_{ij}^R = \int \phi_i^*(1) h_{eff}^R(1) \phi_j(1) dv_1$$

and

$$(ij|kl) = \int \phi_i^*(1) \phi_k^*(2) \frac{1}{r_{12}} \phi_j(1) \phi_l(2) dv_1 dv_2 ,$$

where

$$h_{eff}^n(1) = h^R(1) + \sum_{S(\neq R)} (\mathcal{J}^S(1) - \mathcal{K}^S(1)).$$

$h^R(1)$ is the kinetic + potential energy operator, $\mathcal{J}^S(1)$ and $\mathcal{K}^S(1)$ the Coulomb and exchange operator respectively (cf. McWeeny[2]). Now I_{ij} and $(ij|kl)$ can be expressed in terms of the corresponding quantities α_a, β_{ab} and $(ab|cd)$ over AO's χ_a, χ_b etc., where the α's and β's now contain all interactions between different groups and α_a^N and β_{ab}^N are the bare-nuclei quantities $\alpha_a^N = \int \chi_a^* h^R \chi_a dv$ and $\beta_{ab}^N = \int \chi_a^* h^R \chi_b dv$:

$$\left. \begin{aligned}
\alpha_a = \alpha_a^N + &\sum_{S(\neq R)} \Big\{ [(aa|uu) + (aa|vv) - \tfrac{1}{2}(au|au) - \tfrac{1}{2}(av|av)] \\
&+ Y_S \quad [(aa|uu) - (aa|vv) - \tfrac{1}{2}(au|au) + \tfrac{1}{2}(av|av)] \\
&+ X_S \quad [2(aa|uv) (au|av)] \Big\} \\[2ex]
\beta_{ab} = \beta_{ab}^N + &\sum_{S(\neq R)} \Big\{ [(ab|uu) + (ab|vv) - \tfrac{1}{2}(au|bu) - \tfrac{1}{2}(av|bv)] \\
&+ Y_S \quad [(ab|uu) - (ab|vv) - \tfrac{1}{2}(au|bu) + \tfrac{1}{2}(av|bv)] \\
&+ X_S \quad [2(ab|uv) - \tfrac{1}{2}(au|bv) - \tfrac{1}{2}(av|bu)] \Big\}
\end{aligned} \right\} \quad (3)$$

a and b denote here the AO's χ_a^R and χ_b^R involved in bond R, u and v the AO's χ_u^S and χ_v^S involved in bond S.

The parameters X_S and Y_S are given in terms of the coefficients in equ. (2) by

$$X_S = (c_1^S)^2 - (c_3^S)^3$$
$$Y_S = 2 c_2^S (c_1^S + c_3^S) \tag{4}$$

Y_S represents the amount of charge transferred from orbital v to orbital u in bond S, whereas X_S is associated with the charge density within the bond. This is evident from the one-body density matrix

$$\rho_1^S(1;1') = 2 \int \Phi_S(1,2) \, \Phi_S^*(1',2) \, dx_2,$$

which becomes, after integrating over the spin variables and introducing the quantities $d_{uv}^S(1;1') = \chi_u^S(1) \, \chi_v^S(1')$ etc.

$$P_1^S(1;1') = (1 + Y_S) \, d_{uu}^S(1;1') + (1 - Y_S) d_{vv}^S(1;1') + X_S [d_{uv}^S(1;1') + d_{vu}^S(1;1')] \tag{5}$$

Y_S is expected to be small for bonds of low polarity, being determined essentially by the difference of the electronegativities of the atoms to which u and v are attached, whereas $|X_S|$ is expected to be close to unity for localized bonds. (In fact, preliminary calculations for $H_2C=O$ show that $|X_S| = 0.97$ and $Y_S = 0.08$ for the CH bond; corresponding values for the CO σ bond being 0.94 and 0.19, and for the π bond 0.90 and 0.08). This analysis can easily be extended to include conjugated molecules, i.e. molecules which contain one group of more than two delocalized electrons (π electrons). If we describe the π electron group Q as usual in π electron theories by a one-determinant wave function the α's and β's in the energy expression for this group are still given by equation (3). This shows that the α's and β's defined in (3) are closely related to the corresponding

quantities in the semi-empirical theories of Pariser and Parr[3] and Pople[4], where the neglect of differential overlap and the approximations involved in evaluating the Coulomb integrals $(aa|bb)$ can be justified by assuming that the basis orbitals are orthogonalized AO's (cf. McWeeny[5]). The present formulation therefore suggests a way of calculating the α's and β's in these theories. This would be of interest for example in estimating the difference between the parameters for the nitrogen atom in

$$\text{(pyrrole)} \quad , \quad \text{(pyridine)} \quad \text{and} \quad \text{(pyridinium)} \quad .$$

In the presence of a π electron group Q in the molecule, equation (3) for the α's and β's of the two-electron group R has to be changed into (3'):

$$\alpha_a = \alpha_a^N + \sum_{S(\ne R,Q)} \left\{ [(aa|uu) + (aa|vv) - \tfrac{1}{2}(au|au) - \tfrac{1}{2}(av|av)] \right.$$
$$+ Y_S [(aa|uu) - (aa|vv) - \tfrac{1}{2}(au|au) + \tfrac{1}{2}(av|av)]$$
$$+ X_S \left. [2(aa|uv) - (au|av)] \right\}$$
$$+ \sum_{rs} R_{rs} [2(aa|rs) - (ar|as)]$$

$$\beta_{ab} = \beta_{ab}^N + \sum_{S(\ne R,Q)} \left\{ [(ab|uu) + (ab|vv) - \tfrac{1}{2}(au|bu) - \tfrac{1}{2}(av|bv)] \right.$$
$$+ Y_S [(ab|uu) - (ab|vv) - \tfrac{1}{2}(au|bu) + \tfrac{1}{2}(av|bv)]$$
$$+ X_S \left. [2(ab|uv) - \tfrac{1}{2}(au|bv) - \tfrac{1}{2}(av|bu)] \right\}$$
$$+ \sum_{rs} R_{rs} [2(ab|rs) - (ar|bs)]$$

$$(3')$$

The $\mathbf{R}$-matrix is given in terms of the matrix $\mathbf{T}$ of the π orbital LCAO-coefficients by $\mathbf{R} = \mathbf{T}\mathbf{T}^\dagger$. This shows how - by treating all σ bonds and lone pairs as localized two-electron groups -- the semi-empirical theories of

Pople & Pariser and Parr can be extended to include the σ electron framework explicitly and to treat saturated compounds as well. One possible way would be to calculate all one-electron integrals rigorously (this is quite feasible, because the one- and two-centre integrals can be evaluated in closed form, and the number of three-centre integrals is rather limited) and to get the α^N's and β^N's (over orthogonal hybrid orbitals) by a symmetrical Löwdin orthogonalization. The two-electron integrals, which are very numerous and the evaluation of which is very time consuming, could then be approximated along the lines suggested by Pariser & Parr and Pople.

The formaldehyde molecule was chosen as a first example to compare various approximations with the exact group-function calculations outlined above, largely because the integrals over Slater orbitals are available (Duncan et al.[6]). Programmes have been written and tested

a) to generate the transformation matrix which transforms the original basis into orthogonalized hybrid orbitals localized in the bonds;

b) to transform the one-electron integrals;

c) to transform the two-electron integrals.

d) to perform the group-function calculation in an iterative way by solving the secular equation for each group in turn, starting with $Y=0$ and $X = 1$, until self-consistency is reached.

Several modifications of programme d) have been written to calculate excited states and to treat the π electrons and the oxygen lone-pair electrons together as a four-electron group etc. Programmes b) and c) are completely general, a) and d) can be easily modified and adapted for the calculation of other molecules. No final results have been obtained so far, errors being

suspected in some of the integrals listed by Duncan et al. (Some exchange integrals become negative after the transformation to an orthogonal basis). Some new three-centre integrals are also required in transforming the one-centre integrals to an orthogonal basis. These cancel each other in a molecular orbital treatment and are therefore not given by Duncan. In recent months the main emphasis has therefore been placed on the development of computer programmes for the evaluation of all molecular integrals over Slater orbitals. So far programmes for the evaluation of the following integrals have been written and are in working order:

    (i)   one-centre integrals

   (ii)   two-centre one-electron integrals

  (iii)   two-centre Coulomb integrals

   (iv)   two-centre hybrid integrals

   (v)   three-centre one electron integrals

Programme (i) follows the analysis by Boys[7], programmes (ii) and (iii) that of Roothaan[8]. Programmes (iv) and (v) use two- and three-dimensional numerical integration (cf. Magnusson and Zauli[9]). The Barnett-Coulson method[10] is intended to be used for the remaining integrals, as well as for the three-centre one-electron integrals where it is hoped to be faster than numerical integration; Gauss integration using an 8192 point lattice (16 points for both variables φ and η, 32 for ξ) gives only an accuracy to three figures for a three-centre one electron integral and takes approximately 12 min. Two-dimensional integration using a net of 512 points give a six figure accuracy in the case of hybrid integrals and takes approximately 20 sec.

References.

1) R. McWeeny and K. Ohno, Proc. Roy. Soc., A 255, 367, (1960).

2) R. McWeeny, Rev. Mod. Phys., 32, 335, (1960).

3) R. Pariser and R. G. Parr, J. Chem. Phys. 21, 466, 767 (1953).

4) J. A. Pople, Trans. Faraday Soc., 49, 1375 (1953).

5) R. McWeeny, Proc. Roy. Soc., A 237, 355, (1956).

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2.4) Inter and Intra-Molecular Interactions

The problem of the interaction of two H_2 molecules is being investigated as a first step in the study of more complicated systems (e.g. CH_3 - CH_3 and the related problem of barriers to internal rotations).
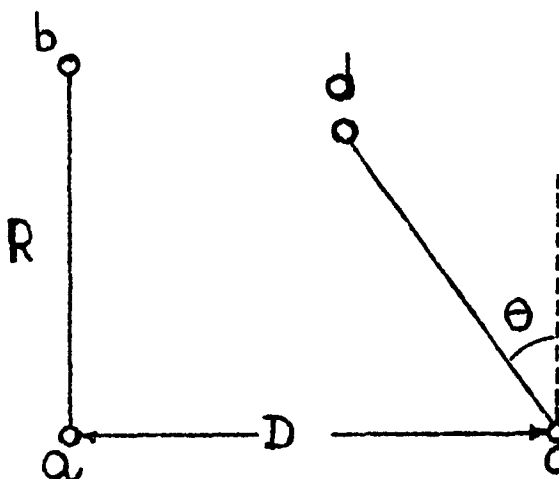
The geometry of the system is illustrated in Figure 1. One molecule is fixed, the other one can rotate around the ac axis keeping the distance $D = R_{ac}$ constant, its state of internal rotation being specified by an angle θ measured from the coplanar position in which the nuclei b,d lie on the same side with respect to the line joining the nuclei a,c- (θ = 0°). R is the equilibrium internuclear distance of a H_2 molecule in its ground state ($^1\Sigma_g$). Our main interest is in values of D ≫ R. As a basis we use 4 atomic orbitals a,b,c,d which have the form:

$$a(1) = \left(\frac{k^3}{\pi}\right)^{1/2} \exp\left(-k\, r_{a1}\right) \, ,$$

i.e. 1s-hydrogen-like AO's centred on the nuclei a,b,c,d. The symbol 1 stands for the three spatial co-ordinates of electron 1, r_{a1} is the distance of electron 1 from the nucleus a, and k is the usual screening constant. We are studying two different approaches to this problem:

A) The energy approach.

B) The force field approach.

A) <u>The energy approach</u>

We assume that the two systems A and B (each consisting of two H nuclei and two electrons) are approximately separated, in the sense that the spatial parts of the wave functions describing the separated molecules from a quantum mechanical point of view do not have an appreciable overlap. The validity of this approximation has been discussed elsewhere.[1][2] Let us suppose that A and B are in their electonic ground state $^1\Sigma_g$, and that we can describe each of them by a "Heitler-London + ionic" wave function of the form:

$$\Phi_A(1,2) = \left[\lambda_1(ab+ba) + \lambda_2\, aa + \lambda_3\, bb\right]\left[\tfrac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\right]$$

$$\Phi_B(3,4) = \left[\lambda_1(cd+dc) + \lambda_2\, cc + \lambda_3\, dd\right]\left[\tfrac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)\right]$$

where Φ_A and Φ_B are individually normalised. We construct the

wave function Ψ for the total system in the form:

$$\Psi(1,2,3,4) = M \, \mathcal{A} \, \phi_A(1,2) \, \phi_B(3,4)$$

where M is a normalization factor and $\mathcal{A}$ is a partial antisymmetrizer, so that Ψ is completely antisymmetric with respect to the exchange of any pair of electrons. We can at this point distinguish between two cases:

I) Strong orthogonal case.

II) Non-orthogonal case.

I) Strong orthogonal case

We start from an ortho-normalized set of AO's

$$\bar{\mathbb{P}} = \left(\bar{a} \; \bar{b} \; \bar{c} \; \bar{d} \right)$$

which may be obtained from the non-orthogonal set $\mathbb{P} = (a\,b\,c\,d)$ by means of a symmetrical orthogonalization:[3]

$$\bar{\mathbb{P}} = \mathbb{P} \, S_p^{-1/2} = \mathbb{P} \, \mathbb{Q}$$

where $S_p = \mathbb{P}^\dagger \mathbb{P}$ is the 4 x 4 overlap matrix in the basis $\mathbb{P}$. We construct ϕ_A from $(\bar{a}\,\bar{b})$ and ϕ_B from $(\bar{c}\,\bar{d})$. In this case the conditions of strong-orthogonality holds:

$$\int \phi_A^*(1,i) \, \phi_B(1,j) \, d\tau_1 = 0 \quad . \; .$$

The Hamiltonian for the system may be written as:

$$H = H_n + H_e$$

$$H_n = \frac{1}{2}\sum_{a,b} G(a,b) \qquad\qquad G(a,b) = R_{ab}^{-1}$$

$$H_e = \sum_{i=1}^{4} \ell(i) + \frac{1}{2}\sum_{i,j} q(i,j)$$

$$\ell(i) = -\frac{1}{2}\nabla^2(i) + V_A(i) + V_B(i) \qquad\qquad q(i,j) = r_{ij}^{-1}.$$

where the symbols have an obvious meaning and atomic units (au) are used throughout. The expectation value for the electronic energy is given by:[4)5)]

$$E_e = E_o^A + E_o^B + C^A + C^B + J^{AB} - K^{AB}.$$

where:

$$E_o^A = \int \left[\ell^A(1)\, P_1^A(1;1')\right]_{1'\to 1} dv_1 + \frac{1}{2}\iint q(1,2)\, P_2^A(12;12)\, dv_1 dv_2$$

$$C^A = \int V_B(1)\, P_1^A(1;1)\, dv_1$$

$$J^{AB} = \iint q(1,2)\, P_1^A(1;1)\, P_1^B(2;2)\, dv_1 dv_2$$

$$K^{AB} = \frac{1}{2}\iint q(1,2)\, P_1^A(2;1)\, P_1^B(1;2)\, dv_1 dv_2.$$

Here $P_1^A(1;1')$, $P_2^A(12; 1'2')$ are respectively the 1-body and the 2-body spinless density matrices for the system A, $P_1^B(1;1')$, $P_2^B(12;1'2')$ the same quantities for the system B. Every term in the preceding

expression for the energy has a very simple physical meaning. For computational purposes it is convenient to write the preceding equation in a matrix form as follows:

$$E_e = tr\ \overline{\mathbb{h}}\ \overline{\mathbb{P}}_1 + \frac{1}{2}tr\ \overline{\mathbb{g}}\ \overline{\mathbb{P}}_2\ ,$$

where 'tr' means "trace", and $\bar{h}$ and $\bar{g}$ are respectively the matrices collecting the 1-electron and 2-electron integrals in the basis $\bar{p}$. They are related to the non-orthogonal basis p by the matrix relations[6]:

$$\overline{\mathbb{h}} = \mathbb{Q}^\dagger\ \mathbb{h}\ \mathbb{Q}$$

$$\overline{\mathbb{g}} = \mathbb{Q}^{(2)\dagger}\ \mathbb{g}\ \mathbb{Q}^{(2)}\ .$$

Here $\mathbb{h}$ is the 4 x 4 matrix of the 1-electron integrals in the basis $\mathbf{p}$ and $\mathbb{g}$ the 10 x 10 2-electron matrix in the same basis (the matrix elements being arranged in a dictionary order). While this method is well adapted to a calculation of the total electronic energy (and easily extensible to more complicated systems), it does not allow for studying explicitly the dependence of the electronic energy on the rotation angle θ.

II) Non-orthogonal case

In this case we use as a basis the set:

$$\mathbb{p} = (a\ b\ c\ d)\ .$$

The electronic interaction energy is given by[7]:

$$E_e^{int} = \frac{C^A + C^B + J^{AB} - K^{AB} + \sum_{n=1}^{2}\left[\ell_n^{AB} + M_n^{AB} - S_n^{AB}(E_o^A + E_o^B)\right]}{1 + \sum_{n=1}^{2} S_n^{AB}}$$

where the terms L_n^{AB}, M_n^{AB}, S_n^{AB} describe the so called "penetration effects" due to the overlap of the electron clouds - E_o^A and E_o^B represent in this case the energies of truly separated systems A and B, and are independent on D. For sufficiently large values of D, the preceding equation may be with a good approximation represented by:

$$E_e^{int} \approx (C^A + C^B + J^{AB} - K^{AB})(1 - S_1^{AB}) + \left[\ell_1^{AB} + M_1^{AB} - S_1^{AB}(E_o^A + E_o^B)\right] + \cdots$$

Using the Mulliken approximation for evaluating the molecular integrals,[3] we find that the total interaction energy takes the form:

$$E = E' + f_1(r) e^{-r} + f_2(r) e^{-2r} + f_3 r^{-1}$$

where $r = R_{bd}$ (au) - E' and f_3 are constant, $f_1(r)$ and $f_2(r)$ are functions involving polynomials in r. Because the variation of f_1 and f_2 with r is much smaller than the exponential one, we can assume $f_1(r)$ and $f_2(r)$ constant with respect to θ and equal to an average value f_1 and f_2. So we get the expression:

$$E = E' + f_1 e^{-r} + f_2 e^{-2r} + f_3 r^{-1}.$$

This expression is closely similar to a preceding relationship found empirically and which allowed to calculate the barrier to internal rotation in ethane-like molecules with a very high degree of accuracy[9]. Calculations for different values of D and θ using the exact equation are in progress for testing the importance of different approximate wave functions and the possibility of approximating the molecular integrals by the Mulliken approximation[8] and bipolar expansion[10]. For comparison the exact calculation of multicentre integrals by the available standard methods[11] [12] is in progress.

B) The force field approach

This approach is based on a theorem due to Hellmann[13] and Feynman[14], which states that the force on a given nucleus in a molecular system is just the classical electrostatic force that would be exerted on this nucleus by the other nuclei and by the electrons regarded as a static charge distribution of density P_1. Once the electron charge distribution has been determined according to the methods of molecular quantum mechanics, the force on a given nucleus in a molecule may be calculated on a purely classical electrostatic basis. If E is the expectative value for the energy of a system with wave function Ψ and Hamiltonian $\mathcal{H}$, we may write:

$$E = \int \Psi^* \mathcal{H} \Psi \, d\tau \qquad \int \Psi^* \Psi \, d\tau = 1$$

$$\frac{\partial E}{\partial \theta} = \int \Psi^* \frac{\partial \mathcal{H}}{\partial \theta} \Psi \, d\tau + 2 \int \frac{\partial \Psi^*}{\partial \theta} \mathcal{H} \Psi \, d\tau ,$$

because $\mathcal{H}$ is hermitean. The second integral in the right-hand side vanishes identically for a stationary state when Ψ is the _exact_ wave function for the system and also when Ψ is a variation function containing suitable parameters.[15] In the present case we simply assume, at first, that this term is small compared with the first.

In this approximation, we get the following expression for the expectation value of the force F_θ acting on the nucleus d:

$$F_\theta = -\frac{\partial E}{\partial \theta} = -\int \Psi^* \frac{\partial \mathcal{H}}{\partial \theta} \Psi \, d\tau = -\int \Psi^* \frac{\partial V}{\partial \theta} \Psi \, d\tau \ ,$$

because the kinetic energy part of $\mathcal{H}$ does not depend on the angle θ. An inspection of the explicit form of the potential energy operator V shows that the only terms which depend upon θ are the nuclear repulsion R_{bd}^{-1} between the nuclei b, d, and the nucleus-electron attraction $-r_d^{-1}$.
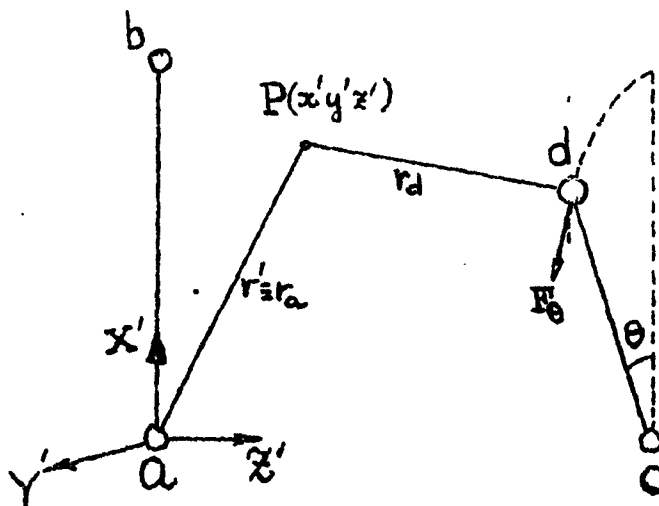
Let us assume a system of co-ordinates as that in Figure 2, and let us separate the force F_θ in the part depending on the nucleus-nucleus interaction and the part depending on the nucleus-electron interaction. We get easily:

$$F_\theta = F_\theta{}^n + F_\theta{}^e$$
$$F_\theta{}^n = R^2 \sin\theta \left[D^2 + 2R^2(1-\cos\theta)\right]^{-3/2}$$
$$F_\theta{}^e = -R \int \Psi^* \left[(x'\sin\theta - y'\cos\theta)r_d^{-3}\right]\Psi\, d\tau .$$

The last expression can be easily simplified introducing the 1-body spinless density matrix $P_1(1;1)$ for the whole system:

$$F_\theta{}^e = -R \int \left[(x'\sin\theta - y'\cos\theta)r_d^{-3}\right] P_1(1;1)\, d\sigma_1.$$

The evaluation of the expectation value for $F_\theta{}^e$ is reduced to the evaluation of a certain number of 1-electron molecular integrals involving 1-, 2-, and 3-centre, and this may be conveniently performed by means of a numerical integration in elliptical co-ordinates.[12] Once $F_\theta{}^e$ has been evaluated for given values of θ, the energy as a function of the angle θ can be obtained by integration.

$$E(\theta) = -\int F_\theta\, d\theta .$$

Work along these lines is in progress for a comparison between the two different approaches.

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ANNEX

to

FTR on Contract No. DA-91-591-EUC-2034, 01-26235-B

I. Personnel Etc.

During the contract period Dr. D. W. Davies has left the Group to take an appointment as Lecturer in Theoretical Chemistry at the University of GrØningen (Netherlands), Dr. B. T. Sutcliffe has joined the Group at M.I.T. (working with Professor Barnett), and Dr. Asgar Ali has been appointed Professor of Physical Chemistry at Presidency College, Calcutta. Dr. Erich Steiner has joined the Group and it is hoped that further appointments will be made during the year.

II. Man hours. Materials, Property

A rough estimate of man hours expended on the project during the contract period is:

Dr. A. Ali	2000 hrs
Dr. D. W. Davies	1000 hrs
Dr. M. Klessinger	2000 hrs
Dr. V. Magnasco	1800 hrs
Dr. B. T. Sutcliffe	2000 hrs
Principal Investigator	300 hrs

Only one of these appointments was provided wholly at contract expense, others being maintained wholly or in part from other sources (Fellowships etc.). No expendable materials were involved apart from those included in overheads (stationary etc.) and no important property was acquired at direct contract expense.

III FUTURE PLANS

During the next contract period 1st November 1962 - 31st Ocyober, 1963 it is hoped that four pieces of work will be concluded:

1) The investigation of the interaction between hydrogen molecules, in a variety of approximations, and of its implications in the theory of barrier heights.

2) The completion of computer programmes for calculations on small molecules, with applications to formaldehyde.

3) The derivation of the spin Hamiltonian which represents the interaction of two electronic systems in the powers of the scalar product of their spins, up to terms in $(S^A . S^B)^3$.

4) The calculation of appropriate self-consistent π-electron polarizabilities for a number of simple conjugated molecules.

Long term projects concerned with general many-electron theory and the correlation problem, and also with the development of computer programmes, will of course continue.